

Side-Chain Crystallinity. V. Heats of Fusion and Melting Temperatures on Monomers Whose Homopolymers Have Long Side Chains

EDMUND F. JORDAN, JR., *Eastern Regional Research Laboratory, Eastern Marketing and Nutrition Research Division, Agricultural Research Service, U.S. Department of Agriculture, Philadelphia, Pennsylvania 19118*

Synopsis

Heats of fusion and melting temperatures were obtained for selected monomeric *n*-alkyl acrylates, *N*-*n*-alkylacrylamides, and vinyl esters. The corresponding thermodynamic parameters for homopolymers, derived from these monomers, had been reported previously from this laboratory. The α -hexagonal crystal modification was indicated near the melting point for the higher *n*-alkyl acrylates, but a β form was stable at low temperatures for the entire series. The magnitude of the heats of fusion indicated β polymorphs for vinyl esters in support of x-ray diffraction analysis from the literature. Because hexagonal crystal geometry prevailed in all reported homopolymers having long side chains, greater emphasis was placed on thermodynamic data for monomers exhibiting this crystal modification. Accordingly, a convergence temperature was estimated statistically for the α -hexagonal crystal modification of these systems and appropriate literature values of the *n*-alkanes and ethyl esters. The convergence temperature was computed to be 135°C, uncorrected for the entropy of disorientation. The anomalously large interfacial end-packing-defect energy of the poly(*n*-alkyl acrylates) and the poly-*N*-*n*-alkylacrylamides was shown to be associated with a high energy barrier to molecular transport in the melt as the vitreous state was approached. In support of this conclusion, similarity of the glass and melting transition temperatures of these homopolymer homologs occurred near their critical side-chain lengths, below which the homopolymers are amorphous. A special critical requirement of nucleus length was not indicated from rough estimations of nucleation parameters for the poly(*n*-alkyl acrylates). These findings lent increased, but still not unqualified, support to an x-ray diffraction study from the literature. The latter had specified the inclusion of the entire side chain and the main-chain units in the crystal lattices of the higher poly(*n*-alkyl acrylates).

INTRODUCTION

Previous publications of this series have presented some limited thermodynamic data on the crystallinity conferred by polymeric units having paraffinic branches. Studies were confined to the crystallinity present in homopolymers¹ and copolymers,² in which crystallinity developed in units having more than a critical side-chain length. Also studied was the influence of this crystallinity on the glass transition³ and mechanical properties⁴ of selected copolymers. In this investigation, some thermodynamic quantities are compiled for the monomers used to prepare the polymers

studied in the above series. These data should complement x-ray studies of the crystal state of vinyl stearate^{5,6} and more recent diffraction measurements on the higher *n*-alkyl acrylates.⁷ More importantly, they should aid in elucidating the as yet elusive nature of the crystal packing in homopolymers derived from these monomers. Before proceeding, however, a brief review of the existing state of knowledge of this area would appear useful, in view of recent, and somewhat conflicting developments.

The heats of fusion and melting points of homologous poly(*n*-alkyl acrylates), poly-*N*-*n*-alkylacrylamides, and poly(vinyl esters), were measured, in a previous study,¹ by differential scanning calorimetry. It was tentatively concluded that crystallinity resided only in portions of the side chains present beyond a certain critical length; the remaining side chains and main-chain units were considered to be amorphous. The critical length varied between 9 and 12 carbon atoms in the bulk homopolymer, depending on the flexibility of the main-chain structure. Evidence for the partial crystallinity of each unit came from the isomorphous nature of mixtures of functionally different homopolymers, and from then narrowing of the calorimetric scanning peaks, as the side-chain length increased in any series. The anomalously large energy requirement for packing chain ends, found for all of the homopolymers, seemed to preclude packing of units along the length designated amorphous,¹ because there should be no extra energy requirement for packing groups terminating as methylene. The insertion of the main-chain units seemed to be excluded in view of the behavior of highly isotactic 1-octadecene, where both the main chain and side chain were incorporated into the crystal lattice. This packing yielded a higher melting point ($\sim 71^\circ\text{C}$)⁸ than was found when these systems were quenched⁸ or were largely atactic.⁹ The atactic homopolymer⁹ melted at 41°C , close to the melting points of many structurally varied C_{16} – C_{18} homopolymers.^{9–14} Plasticization of stiff homopolymers by a nonsolvent¹ raised heats of fusion and melting points, suggesting increased participation of methylene groups in the crystalline array. Of special significance, a long spacing for poly(vinyl stearate)⁶ of about 27 \AA seemed to prohibit the incorporation of total side-chain length and main-chain units into crystalline structures.

Work recently published^{15,16} however, is considerably at variance with the interpretation of limited crystallinity. Flexible C_{18} poly(*n*-alkyl acrylates), whether atactic or significantly isotactic, were shown to have a long spacing in x-ray diffraction measurements of about 47 \AA . This finding was entirely compatible with a lattice including complete side chains. It even suggested the inclusion of main-chain units. Side chains appeared to be packed in a two-layered structure, the chains having a configuration normal to the main chain units. When the main-chain units were bulky, as in the higher poly(*n*-alkyl methylacrylates), main chains were staggered, resulting in lowered heats of fusion and melting temperatures, with the concomitant exclusion of some strands of side-chain methylenes. Of special importance, no amorphous halo was found for the poly(*n*-alkyl acrylates), thus supporting the previous finding on poly(vinyl stearate).¹⁷ These data suggested that homopolymers with flexible long side chains were almost

entirely crystalline. The inclusion of nearly all repeating units in crystallites had been previously estimated¹ from measurements of the heats of fusion obtained by using diluents.

Among areas of agreement, all investigators^{1,6,15,16} have presented evidence that the side chains are arranged normal to the main chain in the α -hexagonal modification characteristic of certain paraffins at their melting point.¹⁸ This packing persists at all undercoolings and remains the stable form at the melting point. In addition, no single work has established the presence of main-chain units in the lattice. However, in view of the findings of Jones⁸ and Aubrey⁹ on 1-octadecene, the exclusion of main-chain units of the polyesters and amides seems to be indicated, at least for atactic or only partially isotactic structures. In view of the new information from the Russian literature, several questions remain concerning the available thermodynamic data.¹ These relate to the abnormally large interfacial energy term for the end packing. This energy can be identified with the intercept of the plot of heat of fusion against side-chain length in homopolymers.¹ The possibility that this energy can be related to a requirement of critical side-chain length is obvious. Whether the critical length is associated with an insurmountable energy barrier to nucleation or whether it is identifiable with transport properties of the melt deserves consideration. Information on this point may be more properly deduced from knowledge of the interfacial term for the corresponding monomers having the same crystal packing.

The purpose of the present work was to determine the heats of fusion, melting points, and the derived entropies of fusion for the same vinyl monomers whose homopolymers were previously studied. Thus, selections of monomers from the homologous *n*-alkyl acrylates, *N*-*n*-alkylacrylamides, and vinyl esters were investigated. Emphasis was placed on the α -hexagonal transition ($\alpha_H \rightarrow l$) of the monomers, when present, because of its relevance to the solid-state structure of the homopolymers. Additionally, data from the literature on alkanes or ethyl esters, having this crystal form stable at melting, were introduced. Parameters, yielding a common convergence temperature by the procedure of Broadhurst,¹⁹ for the hexagonal crystal form of these systems, was estimated by statistical means. Finally, through a comparison of roughly estimated nucleation parameters, derived from a partitioning of the interfacial term of the poly(*n*-alkyl acrylates), with the relative stiffness of the melts at varied chain lengths, a rational explanation of the critical side-chain length required for crystallization was attempted. This accomplished, greater harmony was found in the interpretation of results from differential scanning calorimetry^{1,2} and from x-ray diffraction.^{15,16}

EXPERIMENTAL

Monomers

n-Octyl acrylate, vinyl *n*-octanoate, and vinyl decanoate were from commercial sources; their purities by gas liquid chromatography, GLC, were

97.7%, 97.5%, and 96.1%, respectively. The preparation and purification of the other monomers has been reported.¹ Purities of these by GLC were about 99%, except for tetradecyl acrylate, 84.6%, and *N*-*n*-docosylacrylamide, 85.8%. Purity of each of the monomers used in this study was within the experimental error of elemental analysis. The influence of the impurities (largely nearest-neighbor homologs), when present in individual monomers, was reduced through statistical averaging on plotting the available data.

Calorimetric Procedure

The procedures previously described¹ were followed here, with exceptions as discussed below. The initial deflection of the melting endotherm from the base line was taken as the melting temperature T_m , because the scanning curves were sharp. This procedure tended to compensate for errors introduced by the high scanning rate¹ of 10°C/min; in the case of a few broader curves, peak maxima were taken as marking T_m . While melting points are reported for bulk samples, negligible differences were found between the melting of bulk and crystallized samples. Polymorphic transformations of the higher *n*-alkyl acrylates and *N*-*n*-alkylacrylamides (discussed below in the text) presented difficulties in interpretation of the scans. Melting of the crystal form stable at low temperatures decreased the areas of some of the scans. In some cases, especially with the *n*-alkyl acrylates, this effect, when present in melting endotherms, was absent on freezing. The melting curves could then be corrected. In the *N*-*n*-alkylacrylamides corrections could be applied from the shape of the observed depression in individual scans, coupled with correlations from freezing curves, and from the pattern of behavior of near neighbors in the series. Because of the problems introduced by the premelting of polymorphs, uncertainty of some of the data is reflected in the experimental scatter of their plots.

Refractometric Procedure

Refractometric procedure was as previously described.¹

Computations

An IBM 1130 computer was used for most of the calculations and curve fitting. Convergence temperatures and related parameters were obtained by transforming the variables of the appropriate equation [eq. (3)] for fitting by a linear least-squares program, which computed the parameters and tested them for significance by an analysis of variance.

RESULTS AND DISCUSSION

Heats, Entropies of Fusion, and Melting Points

The thermodynamic data are presented in Table I for all of the systems considered in this investigation. For comparison, thermal data from the

literature are included on the α -hexagonal crystal modification of ethyl esters.^{20a} The entropy quantities are smoothed data, as discussed below. The melting points were obtained by both differential scanning calorimetry and by a careful capillary method involving use of small samples at low heating rates.²¹ The latter were considered to be as accurate as the heat of fusion measurements. A few melting points obtained by refractometry at relatively low heating rates (1°C/30 min)¹ supported the capillary results.

Limited x-ray studies have been conducted by other investigators on certain of the monomers studied in this paper. Vinyl stearate has been shown to be monoclinic at -45°C, with an orthorhombic subcell,⁶ but density-temperature measurements show metastable β forms near room temperature.⁵ The β form is stable at melting,⁵⁻⁷ however. The n -alkyl acrylates (C₁₆, C₁₇, C₁₈) were β -triclinic, but an α -hexagonal modification was stable to about 10°C below the melting point.⁷ However, the β form persisted to melting. No crystallographic data apparently exist for the N - n -alkylacrylamides.

In this work, single calorimetric peaks, both in freezing and melting, were found for all of the vinyl esters, thus supporting the conclusions from the diffraction studies. The hexagonal modification was encountered in the higher ($n = 17-25$, Table I) n -alkyl acrylates on cooling a little below T_m , even at a scanning rate of 10°C/min. However, the transformation to a β form (presumably β -triclinic) was reversible on melting, at the same heating rates. Consequently the melting points in Table I are for the hexagonal modification. Impurities in the monomers, which tend to stabilize hexagonal structures,^{6,18} may have affected the transformation. A single peak in both freezing and melting was found for the lower acrylate members in Table I. Because the energy changes with n were continuous with data for the β -crystal form of the higher members, the β -triclinic modification can be considered characteristic of these monomers also. Single peaks in freezing and melting were also found for the lower N - n -alkylacrylamides ($n = 7-17$), but for the higher members the melting curves were doublets, split by an accompanying exotherm. Freezing curves for the higher members were multi peaked, suggesting complex morphology. The overall energy change (corrected for exotherms) was used to calculate the heats of fusion of the N - n -acrylamides in Table I. Energy changes for all of the amide homologs were continuous functions of carbon length, so that a low-temperature β -crystal form prevailed through the series. As a check on the resolution of the energy changes of the polymorphs in Table I, values of the transformations of ethyl stearate were determined by the same procedures used for the monomers. The literature^{20a} values were obtained.

The relationship between the heats and entropies of fusion and the carbon-chain length, n , fit the equations

$$\Delta H_f(\text{cal/mole}) = \Delta H_{fe} + \alpha n \quad (1)$$

$$\Delta S_f(\text{cal/mole-deg}) = \Delta S_{fe} + \beta n \quad (2)$$

TABLE I
Heats of Fusion, Melting Temperatures, and the Derived Entropies of Fusion for the Monomers and Homopolymers

| Monomer or homopolymer | Carbon length, <i>n</i> | ΔH_f | | ΔS_f | | $T_m, ^\circ\text{C}$ | | Refractometer |
|--|-------------------------|--------------|----------|---------------------------|--------------|-----------------------|-----------|---------------|
| | | cal/g | cal/mole | cal/mole-deg ^a | cal/bond-deg | DSC | Capillary | |
| <i>n</i> -Alkyl Acrylates, $\beta_T \rightarrow \alpha_H \rightarrow l$ Transition | | | | | | | | |
| <i>n</i> -Octyl | 11 | 33.6 | 6,191 | 24.82 | 2.26 | -32.1 | -26.5 | |
| <i>n</i> -Dodecyl | 15 | 42.1 | 10,120 | 35.19 | 2.35 | 1.90 | 4.0 | |
| <i>n</i> -Tetradecyl | 17 | 40.8 | 10,950 | 40.11 | 2.36 | 19.0 | 17.5 | |
| <i>n</i> -Hexadecyl | 19 | 46.6 | 13,820 | 44.93 | 2.36 | 26.0 | 25.0 | |
| <i>n</i> -Octadecyl | 21 | 45.6 | 14,800 | 49.71 | 2.37 | 33.9 | 32.5 | 32.5 |
| <i>n</i> -Docosyl | 25 | 50.5 | 19,220 | 59.08 | 2.36 | 48.9 | 48.5 | |
| <i>n</i> -Alkyl Acrylates, $\alpha_H \rightarrow l$ Transition | | | | | | | | |
| <i>n</i> -Tetradecyl | 17 | 21.3 | 5,718 | 22.03 | 1.30 | 19.0 | 17.5 | |
| <i>n</i> -Hexadecyl | 19 | 27.1 | 8,035 | 26.51 | 1.40 | 26.0 | 25.0 | |
| <i>n</i> -Octadecyl | 21 | 28.7 | 9,314 | 30.85 | 1.47 | 33.9 | 32.5 | 32.5 |
| <i>n</i> -Docosyl | 25 | 33.2 | 12,640 | 39.26 | 1.57 | 48.9 | 48.5 | |
| Poly(<i>n</i> -alkyl Acrylates), $\alpha_H \rightarrow l$ Transition ^b | | | | | | | | |
| <i>n</i> -Dodecyl | 15 | 8.75 | 2,103 | 8.00 | 0.53 | 11.9 | | |
| <i>n</i> -Tetradecyl | 17 | 14.9 | 3,994 | 12.78 | 0.75 | 31.9 | | 25.8 |
| <i>n</i> -Hexadecyl | 19 | 18.2 | 5,394 | 17.27 | 0.91 | 42.9 | | 38.2 |
| <i>n</i> -Octadecyl | 21 | 21.3 | 6,925 | 21.57 | 1.03 | 55.9 | | 50.8 |
| <i>n</i> -Docosyl | 25 | 25.8 | 9,816 | 29.88 | 1.20 | 71.9 | | 66.4 |

SIDE-CHAIN CRYSTALLINITY. V

| | | Ethyl Esters, $\alpha_H \rightarrow l$ Transition ^c | | | | | |
|---|----|--|--------|-------|------|-------|-------|
| | | | | | | | |
| Stearate | 20 | 30.2 | 9,440 | 31.00 | 1.55 | | 33.9 |
| Eicosanoic | 22 | 32.0 | 10,900 | 34.68 | 1.58 | | 41.7 |
| Docosanoic | 24 | 33.6 | 12,400 | 38.30 | 1.59 | | 48.7 |
| Tetradecanoic | 26 | 34.8 | 13,800 | 41.92 | 1.61 | | 54.8 |
| Hexadecanoic | 28 | 35.8 | 15,200 | 45.53 | 1.63 | | 60.2 |
| Tricosanoic | 32 | 37.2 | 17,900 | 52.63 | 1.64 | | 68.5 |
| Tetratricosanoic | 36 | 36.8 | 19,750 | 59.68 | 1.66 | | 75.4 |
| <i>N-n</i> -Alkylacrylamides, Crystal State Unknown | | | | | | | |
| <i>n</i> -Butyl | 7 | 32.3 | 4,108 | 10.93 | 1.56 | 20.9 | 17.3 |
| <i>n</i> -Octyl | 11 | 35.7 | 6,543 | 21.50 | 1.95 | 39.9 | 35.5 |
| <i>n</i> -Dodecyl | 15 | 44.4 | 10,630 | 31.27 | 2.08 | 64.9 | 58.5 |
| <i>n</i> -Tetradecyl | 17 | 43.5 | 11,630 | 36.03 | 2.12 | 64.9 | 64.0 |
| <i>n</i> -Hexadecyl | 19 | 49.6 | 14,660 | 40.69 | 2.14 | 72.9 | 70.5 |
| <i>n</i> -Octadecyl | 21 | 48.7 | 15,760 | 45.34 | 2.16 | 79.9 | 76.0 |
| <i>n</i> -Docosyl | 25 | 50.4 | 19,130 | 54.50 | 2.18 | 86.9 | 82.0 |
| Vinyl Esters, $\beta_M \rightarrow l$ transition | | | | | | | |
| Octanoate | 10 | 30.9 | 5,260 | 21.12 | 2.11 | -34.1 | -29.4 |
| Decanoate | 12 | 33.8 | 6,703 | 25.86 | 2.16 | -13.1 | -9.6 |
| Laurate | 14 | 37.1 | 8,398 | 30.40 | 2.17 | 5.9 | 5.6 |
| Palmitate | 18 | 41.9 | 11,830 | 39.15 | 2.18 | 24.9 | 27.1 |
| Stearate | 20 | 43.3 | 13,440 | 43.44 | 2.17 | 37.9 | 36.8 |
| | | | | | | | 34.4 |

^a Smoothed values calculated by using eqs. (2) and (3).

^b Heats of fusion and melting temperatures taken from Jordan et al.¹

^c Heats of fusion and melting temperatures taken from Lutton.^{20a}

where α and β represent the contributions of each added methylene group to the heats of fusion and entropy, respectively. In this paper n denotes the total carbon length; n_s is the carbon length of the alkyl group. The negative interfacial energy terms ΔH_{fe} and ΔS_{fe} express the defect energy for packing chain ends, because of reduced van der Waals interaction in the planar regions.^{22,23} Values of the parameters are given in Table II. The negative enthalpy term increased as methyl was replaced by the bulkier functional groups of the series. Greater defect energy was found for the hexagonal modifications than was observed for those forms having tighter crystal packing. Tighter packing is also associated with the large values of α , as can be seen. The anomalously large ΔH_{fe} for the poly(*n*-alkyl acrylate) is characteristic of the homopolymers derived from these monomers.¹ This will be considered in the sections below. The value of α for the vinyl esters was similar to that of the higher *n*-alkanes¹⁸ for n , between 11 and 13 (867 cal/mole CH₂). This value for the *n*-alkanes was found by the same curve-fitting procedure used for the data in Table II. Both sets of compounds have an orthorhombic subcell.^{6,18}

The melting points for each series (necessarily equal to $\Delta H_f/\Delta S_f$) were greatly influenced by the magnitude of the entropy parameters of Table II. When β was large and ΔS_{fe} small, melting points tended to be low. This was true for the vinyl esters and the melting of the β form of the acrylates. In contrast, hexagonal melting for both monomeric and polymeric *n*-alkyl acrylates was largely determined by the large value found for ΔS_{fe} ; in the polymers this even overcame the influence of ΔH_{fe} and produced higher melting points than were found for the parent monomers. In analogous fashion, small entropy values for the *N*-*n*-alkylacrylamides (specified by large ΔS_{fe}) and their relatively large enthalpy values (from small ΔH_{fe}) were responsible for the higher melting points found. These data suggest that a low liquid-state entropy determined the melting in both the acrylate polymers and in the amide monomers. This phenomenon was further reflected in the entropies computed on the basis of calories per bond in Table I. Here amide values were as low as those for the esters of hexagonal habit but drifted upward as the polar end unit was successively diluted by increasing numbers of methylene groups.

Convergence Temperature of the Hexagonal Modification

It has long been known, principally from the work of Garner and co-workers²⁴⁻²⁸ and in reviews of subsequent work,^{20b,29} that the melting points of alkane chains substituted at only one end converge to a common value, as the carbon chain becomes infinitely long. This is essentially the melting point of a crystal composed of fully extended chains of linear polymethylene. The relation; which assumes linearity in both enthalpy and entropy, as functions of n , has the form

$$T_m = (\Delta H_{fe} + \alpha n) / (\Delta S_{fe} + \beta n) = T_{m0}(n + a) / (n + b) \quad (3)$$

TABLE II
Parameters for Various Equations

| System | Equations (1) and (2) | | Equation (3) | |
|---|----------------------------|------------------------------------|-----------------------------|----------|
| | Intercept, cal/mole | Slope, cal/mole CH ₂ | <i>T</i> _{m0} , °K | <i>b</i> |
| | Heats of Fusion | | | |
| <i>n</i> -Alkanes, α _H → <i>l</i> ^a | -2939.0 ± 422.8 | 734.9 ± 29.3 | 408.0 | -2.161 |
| <i>n</i> -Alkyl acrylates, β _T → α _H → <i>l</i> | -3975.0 ± 855.5 | 916.2 ± 46.2 | | |
| <i>n</i> -Alkyl acrylates, α _H → <i>l</i> | -6831.0 ± 1036.0 | 776.6 ± 47.5 | 408.0 ^c | -1.075 |
| Poly(<i>n</i> -alkyl acrylates), α _H → <i>l</i> | -9646.0 ± 574.8 | 791.6 ± 27.80 | 408.0 ^c | -7.291 |
| Ethyl esters, α _H → <i>l</i> ^b | -4601.0 ± 192.8 | 705.6 ± 7.52 | 408.0 ^c | -2.817 |
| <i>N</i> - <i>n</i> -Alkylacrylamides | -3191.0 ± 828.6 | 902.8 ± 44.69 | 410.2 | 2.902 |
| Vinyl esters, β _M → <i>l</i> | -3137.0 ± 183.9 | 828.6 ± 12.06 | 406.9 | -1.097 |
| | Entropies of Fusion | | | |
| <i>n</i> -Alkanes, α _H → <i>l</i> | 0.992 ± 0.118 ^d | 1.84 ± 0.004 ^e | | |
| <i>n</i> -Alkyl acrylates, β _T → α _H → <i>l</i> | -1.66 ± 0.54 ^d | 2.44 ± 0.03 ^e | | |
| <i>n</i> -Alkyl acrylates, α _H → <i>l</i> | -17.52 ± 1.09 ^d | 2.30 ± 0.06 ^e | | |
| Poly(<i>n</i> -alkyl acrylates), α _H → <i>l</i> | -24.39 ± 0.74 ^d | 2.18 ± 0.04 ^e | | |
| Ethyl esters, α _H → <i>l</i> | -4.73 ± 0.16 ^d | 1.79 ± 0.01 ^e | | |
| <i>N</i> - <i>n</i> -Alkylacrylamides | -5.33 ± 0.53 ^d | 2.41 ± 0.03 ^e | | |
| Vinyl esters, β _M → <i>l</i> | -0.933 ± 0.33 ^d | 2.23 ± 0.02 ^e | | |

^a Data of Broadhurst.¹⁸

^b Data of Lutton.^{20a}

^c The value of *T*_{m0} found for the *n*-alkanes was fixed for these systems, and values of *a* and *b* only were searched.

^d In cal/mole-deg.

^e In cal/mole-deg-CH₂.

where $T_{m0} = \alpha/\beta$ at $n \rightarrow \infty$ is the convergence temperature and a and b are constants. Equation (3) applies only to crystals of the same geometry. While linearity with n for enthalpy is generally recognized,^{19,22} linearity of entropy with n is impossible,²² even when the temperature dependence of T_{m0} is considered.¹⁹ A correction term, based on consideration of the entropy of destruction of layered packing,²² can be applied, but its application requires extensive experimental data.²³ In spite of these shortcomings, eq. (3) should be accurate over a wide range in the experimental region, and yield melting points low by only a few degrees, as T_{m0} is approached at large n . Because information on the melting temperature of the hexagonal crystal modification over ranges of n is relatively scanty, except for some data on n -alkanes,¹⁸ eq. (3) was applied to the capillary (or refractometric) melting temperatures of Table I.

Values of a , b , and T_{m0} for the hexagonal modification of each set in Table I were obtained by least-squares curve fitting. Values of T_{m0} for each series fell close to the value (408.0°K) resulting from the abundant data on n -alkanes compiled by Broadhurst.¹⁸ Consequently, T_{m0} was set equal to 408.0°K and values of a and b were recomputed for the other systems. Values of the parameters are given in Table II. The convergence temperature for hexagonal packing is only hypothetical; hexagonal polymethylene is unknown. However, the value of 408.0°K lies close to that predicted if one extrapolates limiting free energy of fusion-temperature curves reported for hexagonal n -alkanes.²³ As a check on the computing program, melting points ($\beta_0 \rightarrow l$) for the n -alkanes were curve-fitted in the range $n = 11$ through 100 (by using calculated values for $n < 44$);²² parameters equal to those obtained by Broadhurst¹⁹ resulted. Included in Table II are parameters of the vinyl esters and the N - n -alkylacrylamides. Here T_{m0} was obtained in the computation. Comparison of calculated and found values is presented for the α -hexagonal transition in Table III. Agreement was close, lending support to the utility of the parameters of Table II for estimating T_m over considerable ranges of n with reasonable accuracy. Such computed melting points were consequently used with enthalpy data [calculated by eq. (1)] to calculate the entropy values listed in Table I.

Nucleation and Transport Properties of the Poly(n -Alkyl Acrylates)

As discussed in the introduction, recent x-ray information has suggested^{15,16} that the side chains in the higher poly(n -alkyl acrylates) are entirely crystalline. One of the difficulties with the model proposed by the Russian workers is that the planar interfacial regions are considered to be composed of methyl groups. As can be seen from the value of ΔH_{fe} for n -alkanes (Table II), the defect energy for this end packing in the hexagonal crystal is relatively small. However, that for the poly(n -alkyl acrylates) is large. Jones⁸ considered this same model as possible for the type 1 crystal structure of the isotactic higher 1-alkenes. However, she suggested the main chains as constituting regions of chain ends. This proposal should

TABLE III
Comparison of Melting Points Calculated by Equation (3) with Found Values^a

| <i>n</i> | <i>n</i> -Alkanes $\alpha_H \rightarrow l$ | | <i>n</i> -Alkyl acrylates $\alpha_H \rightarrow l$ | | Poly(<i>n</i> -alkyl acrylates) $\alpha_H \rightarrow l$ | | Ethyl esters, $\alpha_H \rightarrow l$ | |
|----------|---|-------|---|-------|--|-------|---|-------|
| | Calcd | Found | Calcd | Found | Calcd | Found | Calcd | Found |
| 11 | 248.2 | 247.6 | 245.9 | 246.5 | | | | |
| 15 | 282.7 | 283.0 | 277.6 | 277.0 | | | | |
| 17 | 294.9 | 295.0 | 289.2 | 290.5 | 298.1 | 298.9 | | |
| 19 | 305.0 | 305.2 | 298.9 | 298.0 | 312.4 | 311.2 | | |
| 21 | 313.4 | 313.4 | 307.2 | 305.5 | 323.5 | 323.9 | 314.9 | 314.7 |
| 22 | 317.1 | 317.2 | | | | | 321.9 | 321.7 |
| 24 | 323.7 | 323.7 | | | | | | |
| 25 | 326.6 | 326.7 | | | | | | |
| 26 | 329.4 | 329.5 | 320.4 | 321.5 | 339.4 | 339.4 | 327.8 | 327.9 |
| 28 | 334.4 | 334.4 | | | | | 333.0 | 333.2 |
| 32 | 342.6 | 342.5 | | | | | 341.6 | 341.5 |
| 36 | 349.3 | 349.0 | | | | | 348.5 | 348.4 |
| 39 | 353.4 | 353.5 | | | | | | |
| 43 | 358.1 | 358.5 | | | | | | |

^a Calculated by using the parameters of Table II with T_{m0} of 408.0°K, found for the *n*-alkanes, fixed for the others.

produce greater defect energy than that found for alkanes because of the volume requirement of the main-chain helices. However, when the main-chain units are considerably bulkier, as with atactic poly(*n*-alkyl acrylates), it is even questionable whether they are present in the crystallites. In any event, their role in producing planar defects would seem to be at least as great as that of the polymerizable group of the corresponding monomers.

These considerations indicate the importance of considering the relation between the large interfacial energy (ΔH_{fe} , Table II) of the homopolymer homologs and the critical carbon-chain length per unit required before crystallinity commences. This will be considered in the sections below. An effort will be made to ascertain whether this enthalpy quantity is associated with transport properties of the melt, or whether it arises as a critical dimension limitation in the nucleation process. Because only very limited data is available for the computation of the nucleation parameters, these must be considered only rough approximations; the sole purpose of their estimation is to detect, qualitatively, any trends that might specify a critical side-chain length for stable nucleation.

By classical nucleation theory,³⁰⁻³³ the homogeneous rate of formation of a stable primary nucleus from an embryo is governed by two activation processes. Thus, an appropriate relation is

$$I = NkT/h e^{-\Delta F_p^*/kT} e^{-\Delta F_f^*/kT} \quad (4)$$

where I is the steady-state rate of primary nucleation. The quantity ΔF_p^* is the free energy for transport of molecules over a short distance to the surface of the embryo or nucleus. The other activation parameter, ΔF_f^* , defines the energy barrier to forming a nucleus of a critical size. Other quantities in eq. (4) are Boltzman's constant k , Planck's constant h , and Avogadro's number N . The transport process, being proportional to the viscosity of the melt,^{34,35} becomes important at low temperatures. This is especially true in polymers, in the vicinity of their glass transition temperatures, where steady-state activation no longer applies.³⁶ On the other hand, the critical energy barrier to nucleation ΔF_f^* dominates only at relatively small undercoolings. Consequently, because of the competition expressed by ΔF_p^* and ΔF_f^* , the rate of nucleation passes through a maximum as temperature is lowered.

On the assumption that the interfacial enthalpy term for the poly(*n*-alkyl acrylates), ΔH_{fe} , contains a contribution to the enthalpy of nucleation, the intercept of eq. (1) may be partitioned as follows

$$\Delta H_{fe} = \Delta H_{fn} + \Delta H_{feM} + \Delta H_{feR} \quad (5)$$

where ΔH_{fn} is the enthalpy of nucleation, ΔH_{feM} the energy of packing the methyl-terminating endgroup and ΔH_{feR} the energy of packing the bulkier group at the other end of the molecule. If ΔH_n is small for simple compounds, ΔH_{fe} for the *n*-alkanes in Table II may be approximated by $2\Delta H_{feM}$ while ΔH_{fe} for the ethyl and acrylate esters is the sum $\Delta H_{feM} + \Delta H_{feR}$. The minimum carbon-chain length of the unit required for nucleation in

the acrylate homopolymers may be assumed to be the value of n at $\Delta H_f = 0$. This quantity, n^* , is given by¹

$$n^* = \Delta H_{fe}/\alpha \quad (6)$$

The starred quantities will be designated "critical" quantities in this discussion. The energy assumed to be associated with the nucleation process in the poly(n -alkyl acrylates) is, therefore

$$\Delta H_{fn} = \Delta H_{fePOA} - \Delta H_{feOA} \quad (7)$$

where POA and OA represent poly(octadecyl acrylate) and monomeric octadecyl acrylate, respectively. This quantity is -2815 cal/mole CH_2 . If crystallinity resides in only the total length of the side chains of any homologous series of homopolymers,^{15,16} a convenient factor may be defined as

$$-f = (\Delta H_{fn}/\Delta H_{fe})_{POA} = -0.2918 \quad (8)$$

The enthalpy of fusion of each side-chain methylene group [α in eq. (1)], expressed in ergs/cm³, may now be corrected for the energy of nucleation by

$$\Delta H_{fc} = -f\Delta H_{fe}/[(f'\Delta H_{fe}/\alpha)V_n] + \alpha/V_n \quad (9)$$

where ΔH_{fc} is the corrected enthalpy and f' is another factor, which reduces the intercept ΔH_{fe} of the unit-chain-length relation, eq. (1), to a value relating to side chains only.¹ The factor f' is given by

$$f' = (14.026n + 1.01)/\text{MW}_{\text{unit}} \quad (10)$$

and V_n is the volume fraction of a methylene group ($16.17 \text{ cm}^3/\text{mole}$).³⁷

With the nucleus geometry considered as a cylinder, with the length l_0 fixed³⁰ by the contour length of the side chains [$(n_s/2) 2.54 \times 10^{-8} \text{ cm}$] and with a variable critical radius r^* for the free-energy surface,³⁰ the expressions derived by Hoffman³⁸ were used. These described the analogous case of a nucleus length, fixed as the radius varied, over a confined range of undercooling. The expressions used to calculate the nucleation parameters, listed in Table IV, are³⁸

$$\Delta F_c = \Delta H_{fc}(\Delta T/T_m) \quad (11)$$

$$r^* = \delta_s/\Delta F_c \quad (12)$$

$$\delta_e = l_0\Delta F_f/4.0 \quad (13)$$

$$\Delta F_c^* = \pi l_0 \delta_e^2/\Delta F_c \quad (14)$$

where ΔH_{fc} is from eq. (9); ΔF_c is the corrected free energy of fusion, in ergs/cm³; δ_s , the side free energy of the cylinder, is taken as 9.64 ergs/cm^2 (as was calculated for n -octadecane and used as the side-surface free energy of polyethylene³⁹), and δ_e is the end-surface free energy, in ergs/cm². The undercooling ΔT was an average value, 8.8°C for the poly(n -alkyl acry-

TABLE IV
Nucleation Parameters Estimated by the Use of Equations (9)-(14)

| Parameters ^a | Poly(<i>n</i> -alkyl acrylates), $n_s - n_s^{*b,c}$ | | | | | <i>n</i> -Alkanes, $n - n^{*b,c}$ | | | | |
|--|--|------|------|------|------|-----------------------------------|------|------|------|------|
| | 2.8 | 4.8 | 6.8 | 8.8 | 12.8 | 3.0 | 5.0 | 7.0 | 9.0 | 13.0 |
| $\Delta H_f \times 10^{-8}$, ergs/cm ³ | 12.0 | 12.4 | 12.6 | 12.8 | 13.1 | 13.5 | 13.5 | 13.5 | 13.5 | 13.5 |
| $\Delta F \times 10^{-8}$, ergs/cm ³ | 0.37 | 0.36 | 0.35 | 0.34 | 0.34 | 0.87 | 0.73 | 0.65 | 0.60 | 0.55 |
| $r^* \times 10^8$, cm | 26.0 | 27.0 | 27.5 | 28.1 | 28.9 | 11.1 | 13.3 | 14.8 | 16.0 | 17.6 |
| $l_0 \times 10^8$, cm | 15.2 | 17.8 | 20.3 | 22.9 | 27.9 | 8.9 | 11.4 | 14.0 | 16.5 | 21.6 |
| δ_0 , ergs/cm ² | 1.41 | 1.59 | 1.78 | 1.96 | 2.34 | 1.92 | 2.07 | 2.27 | 2.49 | 2.96 |
| $\delta_s^2 \delta_0$, ergs ³ /cm ⁶ | 131 | 148 | 165 | 182 | 218 | 178 | 192 | 211 | 231 | 275 |
| $\bar{\delta}_0$, ergs/cm ² | 5.1 | 5.3 | 5.5 | 5.7 | 6.0 | 5.6 | 5.8 | 5.9 | 6.1 | 6.5 |
| $\Delta F^* \times 10^{-8}$, ergs | 12.0 | 14.5 | 16.9 | 19.5 | 24.3 | 3.0 | 4.6 | 6.3 | 8.0 | 11.5 |

^a Model of the nucleus was taken to be a cylinder. The side surface free energy δ_s was assumed to be 9.64 erg/cm², as was found experimentally for *n*-octadecane.³³

^b The undercooling ΔT was an average value of 8.8°C for the poly(*n*-alkyl acrylates); for the *n*-alkanes the undercooling selected³³ was 12°C. Melting temperatures are from Table I.

^c The critical minimum length of the side-chain nucleus n_s^* was calculated¹ by $\Delta H_f/\alpha$ to be 9.2 for the poly(*n*-alkyl acrylates); the minimum nucleus length was calculated to be 4.0 for the *n*-alkanes by eq. (6).

lates). It was the temperature difference between the melting point and freezing point at the experimental scan rate of 10°C/min. Deviation from this value for individual polyesters were small. The undercooling ΔT for the parameters of the n -alkanes in Table II [calculated by using eq. (9)] was taken as 12°C; this is the approximate temperature of the isothermal rate maximum found for certain n -alkanes.³³ In view of the large temperature coefficient for the nucleation of n -alkanes, the error in this arbitrary selection is thought to be small. Included in Table II, for comparison with other reported data,³⁰ are the saddle-point surface-free-energy parameter $\delta_s^2\delta_e$ and the mean interfacial-free-energy term $\bar{\delta}$. Again, for purposes of comparison, the poly(n -alkyl acrylates) and n -alkanes were taken at similar values of $(n^* + n)$.

The parameters in Table IV are all reasonable values,^{30,33,38} even though δ_e may be a little large (~ 0.5 erg/cm² has been estimated for some compounds³⁸). The upward drift in δ_e with side-chain length in both systems probably resides in the uncertainty in ΔT ; small changes in the undercooling with change in n would compensate for the drift. Both the homopolymer and n -alkanes have similar values for the parameters, even though the difference in carbon lengths of the two systems is about 8 methylene groups. The significant fact to emerge from these approximate values is that no special tendency toward intrinsically unstable nuclei or unrealistic radii sizes are to be found as the critical length ($n^* - n = 0$) is approached. Consequently, a critical side-chain length, below which nuclei would be unstable at all undercoolings, is not specified. These data suggest that lowered rates of diffusion to nucleus sites may be responsible for the retardation of crystallization for chains shorter than n^* .

Figure 1 shows a plot of the glass and melting temperature for the poly(n -alkyl acrylates) versus their side-chain length n_s . T_g values are from an

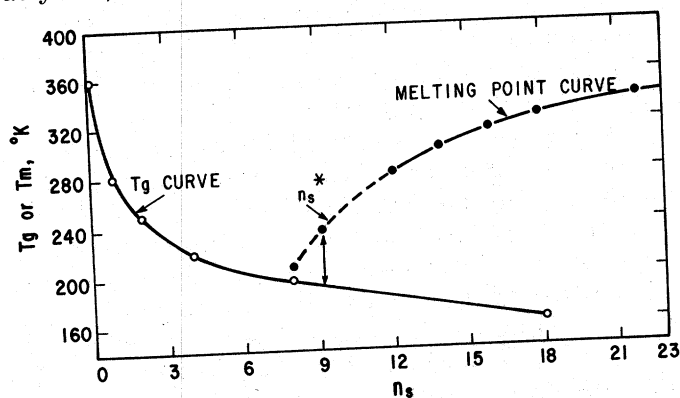


Fig. 1. Plot of the glass transitions T_g and the melting temperatures T_m for the homologous poly(n -alkyl acrylates) vs. the number n_s of methylene groups (including terminal methyl) in the side chain. The temperature difference between the melting curve and the T_g curve at the critical side-chain length below which crystallinity is absent in homologs, n_s^* , is indicated by the double arrow. Melting points were calculated by using eq. (3).

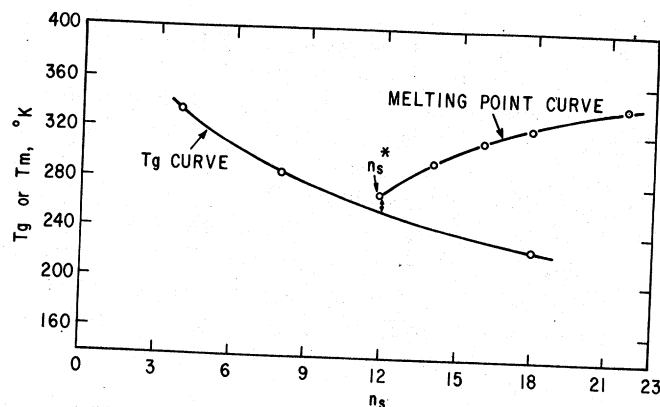


Fig. 2. Plot of the glass transitions T_g and the melting temperatures, T_m for the homologous poly(*N-n*-alkylacrylamides) vs. the number n_s of methylene groups (including terminal methyl) in the side chain. The temperature difference between the melting curve and the T_g curve, at the critical side chain length below which crystallinity is absent in homologs, n_s^* , is marked by the double arrow.

earlier study.³ The curves tend to intersect in the neighborhood where $n_s^* \sim 9.2$ (double arrow). This is the value of n_s of homologs below which crystallinity has been shown to be absent.¹ Similarly, in Figure 2, melting points and glass transition temperatures approach closely at n_s of 12 for the *N-n*-alkylacrylamides. For this system n_s^* is 12.¹ The difference between T_m and T_g is greater for the acrylates than for the *N-n*-alkylacrylamides (relative heights of the double arrows in Figures 1 and 2). It is pertinent that the extent of crystallinity at $n'_s - n_s^* = 2.8$ was higher for the polyacrylates than for the poly(*N-n*-alkylacrylamides).¹ The plots constitute strong evidence that the observed retardation of nucleation in the homopolymers having long side chains is produced by a high energy barrier to molecular transport [ΔF_p^* in eq. (4)] rather than by a critical dimension requirement for nucleation (ΔF_f^* in the same equation). The anomalously large interfacial energy term (ΔH_{fe} , Table II) of eq.(1), consequently, appears to arise as a defect energy associated with a retarded rate of molecular diffusion as the glass transition is approached. The temperature of the approach to the vitreous state is controlled by the free volume available in polymeric systems of varied structures. Thus restrictions on movement of the side chains, imposed by stiffness in the main chains of homopolymers, appear to determine the critical side-chain length required for effective nucleation. This, in turn, governs the increase in magnitude of the intercept in eq. (1) for any given polymer structure relative to its monomer. It may be concluded that inclusion of total side chains in crystallites, as is clearly specified in recent literature,^{15,16} produces an additional reduction in internal energy associated with a barrier to molecular transport, over the defect energy of packing groups larger than methylene. Consequently, the inclusion of all groupings in the polymer unit are not energetically excluded from crystallites provided the critical side-chain length has been exceeded.

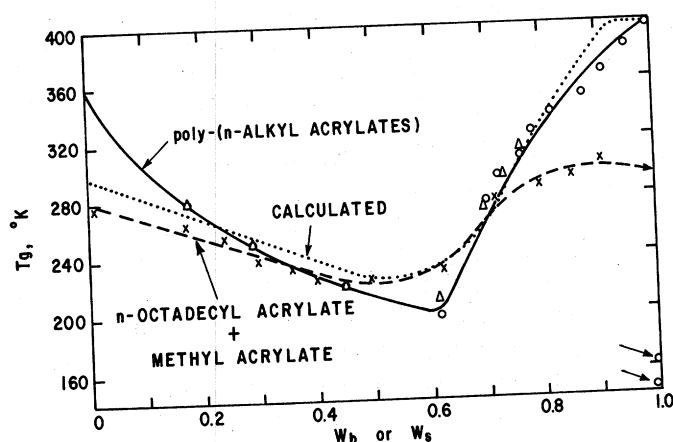


Fig. 3. Influence of side-chain crystallinity on T_g for the homologous poly(*n*-alkyl acrylates), (—) plotted as T_g vs. the weight fraction w_s of side chain per homopolymer unit; values of T_g for the crystalline homopolymers were calculated by using eq. (15); (Δ) literature values of T_g .⁴⁰ Comparison is shown with (---) data for copolymers of *n*-octadecyl acrylate and methyl acrylate³ plotted as the weight fraction of *n*-octadecyl acrylate w_b ; (...) calculated for the poly(*n*-alkyl acrylates) by using eq. (16). Arrows indicate the T_g of (top) amorphous poly(*n*-octadecyl acrylate); (bottom) polyethylene.

Opposing the inclusion of main chain units, however, is the seeming isomorphic behavior of homopolymer mixtures and the other evidence discussed in the introduction.

Effect of the Glass Transition on the Development of Side-Chain Crystallinity in Homopolymers and Copolymers

The rate-controlling limitation imposed by difficulties in molecular transport, discussed above in connection with homopolymers, seemed to apply equally well in determining the onset of crystallinity in copolymers. This may be seen from the plots in Figure 3. The solid line is a plot of the glass transition temperature for the poly(*n*-alkyl acrylates) versus the weight fraction of the side chain of each homolog w_s . The T_g values are from a previous paper;³ those at the right ($w_s > 0.6$), in the region where side-chain crystallinity is causing the apparent T_g to rise, were computed from the empirical equation

$$T_g = T_m - 12^\circ \quad (15)$$

This relation was obtained, partially, by a correlation of onset temperature for poly(*n*-octadecyl acrylate)³ with an averaging of the onset temperatures of the fusion curves for other homopolymers exhibiting side-chain crystallinity. Literature values of T_g ,⁴⁰ shown in the figure as triangles, lie close to the line. These lend support to the validity of eq. (15). The value of T_g at $w_s = 1.0$ is for hypothetical hexagonally crystallized polymethylene. This plot may be compared with one (dashed line) for copolymers of *n*-octadecyl acrylate and methyl acrylate.³ The T_g values are plotted here

against the weight fraction of *n*-octadecyl acrylate, designated w_b . The superficial resemblance of the two curves is obvious. Thus, the onset of crystallinity occurred in both systems at w_s or w_b of 0.5 or 0.6. In a previous publication³ it was demonstrated that the onset of crystallinity, due to units of *n*-octadecyl acrylate in copolymers, was a function of the specific vitreous state of the copolymers; the lower the glass transition, the smaller the value of w_b required to initiate crystallinity. Generally the critical temperature difference ($T_m^* - T_g^*$) below which crystallinity is prevented³ at all undercoolings is 25–40°C. Again, a common requirement of both homopolymers and copolymers appears to be a critical free volume in the melt, which specifies the attainment of sensible rates of nucleation. On extending these principles to the case of simple *n*-alkanes, their weak glass-forming tendency^{33–35} can be associated with the excellent mobility of their melts at all but the most extreme undercoolings. Thus, free, short-chain linear alkanes can be considered to represent the limiting case of the behavior of alkane side chains, restricted in their movement by attachment to polymeric main chains.

An empirical equation was described in a previous publication³ for predicting the T_g of copolymers containing *n*-octadecyl acrylate, over all compositions. It satisfactorily expressed the rise in apparent T_g as side-chain crystallinity developed. The equation was

$$T_g = w_a T_{ga} + [w_b' + (w_c' - w_c'^{C+k_s w_b})] T_{gb} + (w_c'^{C+k_s w_b}) T_{gc} \quad (16)$$

where T_{ga} is the T_g of the amorphous homopolymer T_{gb} is the glass transition of the amorphous state of the unit exhibiting side-chain crystallinity, and T_{gc} is the observed glass transition. C and k_s were constants having the values 4.0 and -4.0 , respectively. The weight fraction of amorphous homopolymer is w_a , and $w_b = w_b' + w_c'$. The weight fraction of crystallizable comonomer is w_b , and w_b' and w_c' are the portions of w_b that are amorphous and crystalline, respectively. These quantities are related to the ratio of the actual extent of crystallinity, to the maximum possible at equilibrium,² $x_c/x_{c,max}$, by the relations

$$w_c' = [(x_c/x_{c,max})_0 + A w_b + B w_b^2] w_b \quad (17)$$

$$w_b' = 1 - w_c'.$$

For stiff amorphous homopolymers, $(x_c/x_{c,max})_0$, A , and B were 0.1030, -0.3567 , and 1.290 , respectively. This equation [eq. (16)], applied to the data for the homopolymeric poly(*n*-alkyl acrylates), with w_b replaced by w_s , is shown as the dotted line in the figure. For this calculation T_{ga} was taken as 300°K, T_{gb} , the value accepted for hypothetical linear amorphous polyethylene, -130°C^{41} (lower arrow in the figure) and T_{gc} is from the convergence temperature, 408.0°K, through eq. (15), giving 123°C as T_{gc} . Agreement with experimental values is close enough to indicate the general utility of this equation in predicting the T_g of copolymers and homologous homopolymers in the amorphous region, as well as apparent values as T_g .

is influenced by the development of side-chain crystallinity. This agreement again emphasizes the common origins of the morphological behavior of systems containing long side branches.

SUMMARY AND CONCLUSIONS

Heats, entropies of fusion, and melting temperatures were obtained for three homologous series of monomers. Comparison was made of the thermodynamic data with similar data for homopolymers reported previously. Because the hexagonal crystal geometry prevails in homopolymers, monomeric systems exhibiting this crystal structure were more extensively studied. In keeping with this purpose the useful range of the data was extended by obtaining convergence temperatures for hypothetical hexagonal linear polymethylene for all systems exhibiting this crystal form at melting. The metastable hexagonal convergence temperature was estimated to be 408.0°K for these systems. The effect of stiffness of the melt on the diffusion of segments to a crystal nucleus was considered to determine the critical side-chain length required for the onset of crystallinity. Diffusional factors appeared to determine the onset of crystallinity of both homopolymers and copolymers at all undercoolings. These imposed an additional reduction in internal energy in homopolymers. Consequently, the inclusion of total side chain and main chain units in crystallites, specified by recent x-ray data from the literature, is not energetically excluded, provided the critical side-chain length has been exceeded. However, the extant thermal data still seem to exclude main-chain units from crystallites.

The authors thank Mrs. Ruth Zabarsky for the operation of the computer, Dr. Clyde L. Ogg and Mrs. Annette S. Kravitz for the elemental analysis, Mr. Donald W. Feldeisen for the refractometric melting points, and Mr. John W. Pensabene for the analysis of the monomers by gas liquid chromatography. The authors express their special thanks to Dr. C. Roland Eddy, Mrs. Virginia Metzger, and Mr. Paul Gormisky for the computer program which calculated the convergence temperature parameters.

Reference to brand or firm name does not constitute endorsement by the U.S. Department of Agriculture over others of a similar nature not mentioned.

References

1. E. F. Jordan, Jr., D. W. Feldeisen, and A. N. Wrigley, *J. Polym. Sci. A-1*, **9**, 1835 (1971).
2. E. F. Jordan, Jr., B. Artymyshyn, A. Specca, and A. N. Wrigley, *J. Polym. Sci. A-1*, **9**, 3349 (1971).
3. E. F. Jordan, Jr., *J. Polym. Sci. A-1*, **9**, 3367 (1971).
4. E. F. Jordan, Jr., G. R. Riser, B. Artymyshyn, J. W. Pensabene, and A. N. Wrigley, *J. Polym. Sci. A-2*, **9**, 1657 (1971).
5. E. R. Fitzgerald, *J. Chem. Phys.*, **32**, 771 (1960).
6. N. Morosoff, H. Morawetz, and B. Post, *J. Amer. Chem. Soc.*, **87**, 3035 (1965).
7. B. S. Petrukhin, V. P. Shibaev, and N. A. Plate, *Polym. Sci. USSR*, **12**, 776 (1970).
8. A. T. Jones, *Makromol. Chem.*, **71**, 1 (1964).
9. D. W. Aubrey and A. Barnatt, *J. Polym. Sci. A-2*, **6**, 241 (1968).

E. F. JORDAN, JR.

10. R. H. Wiley and G. M. Brauer, *J. Polym. Sci.*, **3**, 647 (1948).
11. S. A. Greenberg and T. Alfrey, *J. Amer. Chem. Soc.*, **76**, 6280 (1954).
12. C. G. Overberger, C. Frazier, J. Mandelman, and H. F. Smith, *J. Amer. Chem. Soc.*, **75**, 3326 (1953).
13. W. S. Port, J. E. Hansen, E. F. Jordan, Jr., T. J. Dietz, and D. Swern, *J. Polym. Sci.*, **7**, 207 (1951).
14. E. F. Jordan, Jr., G. R. Riser, B. Artymyshyn, W. E. Parker, J. W. Pensabene, and A. N. Wrigley, *J. Appl. Polym. Sci.*, **13**, 1777 (1969).
15. V. P. Shibaev, B. S. Petrukhin, N. A. Plate, and V. A. Kargin, *Polym. Sci. USSR*, **12**, 160 (1970).
16. N. A. Plate, V. P. Shibaev, B. S. Petrukhin, Y. A. Zubov, and V. A. Kargin, *J. Polym. Sci. A-1*, **9**, 2291 (1971).
17. D. A. Lutz and L. P. Wittnauer, *J. Polym. Sci. B*, **2**, 31 (1964).
18. M. G. Broadhurst, *J. Res. Nat. Bur. Stand.*, **66A**, 241 (1962).
19. M. G. Broadhurst, *J. Chem. Phys.*, **36**, 2578 (1962).
20. E. S. Lutton, in *Fatty Acids*, K. S. Markley, Ed., 2nd ed., Part 3, Interscience, New York, 1967, (a) pp. 2588-2589; (b) pp. 2583-2641.
21. E. L. Skau, J. C. Arthur, H. Wakeham, in *Technique of Organic Chemistry, Physical Methods*, E. Weissberger, Ed., Part 1, 3rd ed., Interscience, New York, 1959, pp. 287-355.
22. P. J. Flory and A. Vrij, *J. Amer. Chem. Soc.*, **85**, 3548 (1963).
23. C. M. L. Atkinson and M. J. Richardson, *Trans. Faraday Soc.*, **65**, 1749 (1969).
24. W. E. Garner, F. C. Madden, and J. E. Rushbrooke, *J. Chem. Soc.*, **1926**, 2491.
25. W. E. Garner and J. E. Rushbrooke, *J. Chem. Soc.*, **1927**, 1351.
26. W. E. Garner and A. M. King, *J. Chem. Soc.*, **1929**, 1849.
27. W. E. Garner, K. Van Bibber, and A. M. King, *J. Chem. Soc.*, **1931**, 1533.
28. A. M. King and W. E. Garner, *J. Chem. Soc.*, **1934**, 1449.
29. A. R. Ubbelohde, *Melting and Crystal Structure*, Clarendon Press, Oxford, 1965, pp. 118-134.
30. L. Mandelkern, *Crystallization of Polymers*, McGraw-Hill, New York, 1964, pp. 215-290.
31. D. Turnbull, *J. Appl. Phys.*, **21**, 1022 (1950).
32. D. Turnbull and J. C. Fisher, *J. Chem. Soc.*, **17**, 71 (1949).
33. D. Turnbull and R. L. Cormia, *J. Chem. Phys.*, **34**, 820 (1961).
34. M. H. Cohen and D. Turnbull, *J. Chem. Phys.*, **31**, 1164 (1959).
35. D. Turnbull and M. H. Cohen, *J. Chem. Phys.*, **29**, 1049 (1958).
36. J. D. Ferry, *Viscoelastic Properties of Polymers*, Wiley, New York, 1961, pp. 201-247.
37. D. W. Van Krevelen and P. J. Hoftyzer, *J. Appl. Polym. Sci.*, **13**, 871 (1969).
38. J. D. Hoffman, J. J. Weeks, and W. M. Murphy, *J. Res. Natl. Bur. Stand.*, **63A**, 67 (1959).
39. R. L. Cormia, F. P. Price, and D. Turnbull, *J. Chem. Phys.*, **37**, 1333 (1962).
40. J. Brandrup and E. H. Immergut, Eds., *Polymer Handbook*, Interscience, New York, III, pp. 66-67.
41. F. C. Stehling and G. Mandelkern, *Macromolecules*, **3**, 242 (1970).

Received July 27, 1972